

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 11 May 2001 (11.05.01)	Applicant's or agent's file reference O/PAPCT146
International application No. PCT/KR00/01051	Priority date (day/month/year) 22 September 1999 (22.09.99)
International filing date (day/month/year) 19 September 2000 (19.09.00)	
Applicant CHUNG, Bong, Jin et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 30 March 2001 (30.03.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38
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DOI 08 FEB 2002

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference O/PAPCT146	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR00/01051	International filing date (day/month/year) 19 SEPTEMBER 2000 (19.09.2000)	Priority date (day/month/year) 22 SEPTEMBER 1999 (22.09.1999)
International Patent Classification (IPC) or national classification and IPC IPC7 A01N 25/14		
Applicant DONGBU HANNONG CHEMICAL CO., LTD. et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30 MARCH 2001 (30.03.2001)	Date of completion of this report 22 JANUARY 2002 (22.01.2002)
Name and mailing address of the IPEA/KR Korean Intellectual Property Office Government Complex-Daejeon, Dunsan-dong, Seo-gu, Daejeon Metropolitan City 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer SEO, Eul Soo Telephone No. 82-42-481-5632

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR00/01051

I. Basis of the report

1. With regard to the elements of the international application:*

- ☒ the international application as originally filed
- ☐ the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____
- ☐ the claims:
pages _____, as originally filed
pages _____, as amended (together with any statement) under Article 19
pages _____, filed with the demand
pages _____, filed with the letter of _____
- ☐ the drawings:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____
- ☐ the sequence listing part of the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language English which is

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☒ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheet _____

5. ☐ This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed." and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR00/01051

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-5	YES
	Claims		NO
Inventive step (IS)	Claims	1-5	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-5	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Reference is made to following documents from the International Search Report(ISR):

D1: JP-A-11-199409

D2: US-A-5635445

D1 discloses water-soluble granule of herbicide composition containing quinclamine and carfentrazone-ethyl as active ingredient. However, this document does not mention paraquat dichloride as active ingredient.

D2 is considered to represent the most relevant state of the art. It discloses granular herbicidal water-soluble composition based either on aminotriazole alone or on aminotriazole combined with at least one other herbicide selected from the group comprising alkaline, paraquat etc. However, this document is silent on granular herbicidal water-soluble composition containing paraquat as major ingredient and its effect.

Claims 1 and 5 are considered to involve an inventive step because they are neither disclosed nor derivable from the disclosures of the cited prior art(Article 33(3) PCT).

Hence, dependent claims 2-4 also involve an inventive step(Article 33(3) PCT)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR00/01051

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
JP-A-11-199409	27-07-99	13-01-98	
US-A-5635445	03-06-97	18-07-95	19-07-94

2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non-written disclosure (day/month/year)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

national application No.

PCT/KR00/01051

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

The term "a small amount of water" used in the description and claim 1, especially when it refers to a range, is vague and unclear, thereby resulting in lack of clarity(Article 6 PCT) when used to interpret the claims.

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O/PAPCT146

PCT REQUEST

Original (for SUBMISSION) - printed on 19.09.2000 11:17:49 AM

0	For receiving Office use only	
0-1	International Application No.	PCT/KR 00/01051
0-2	International Filing Date	19 September 2000 (19.09.00)
0-3	Name of receiving Office and "PCT International Application"	Korean Industrial Property Office PCT International Application
0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.91 (updated 01.07.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Korean Industrial Property Office (RO/KR)
0-7	Applicant's or agent's file reference	O/PAPCT146
I	Title of invention	WATER DISPERSABLE GRANULE COMPRISING PARAQUAT DICHLORIDE AND ITS MANUFACTURING METHOD
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	DONGBU HANNONG CHEMICAL CO., LTD.
II-5	Address:	838, Yeoksam-dong, Kangnam-gu 135-080 Seoul Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	02-3484-1500
II-9	Facsimile No.	02-565-8532
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	CHUNG, Bong Jin
III-1-5	Address:	201, 1092-8, Kalsan-dong, Tongan-gu, Anyang-city, 431-088 Kyungki-do Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

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III-2	Applicant and/or inventor	applicant and inventor
III-2-1	This person is:	US only
III-2-2	Applicant for	
III-2-4	Name (LAST, First)	KIM, Seung Ho
III-2-5	Address:	Mansu KNHC Apt. 214-1402, Mansu 4-dong, Namdong-gu, 405-244 Inchun Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
III-3	Applicant and/or inventor	applicant and inventor
III-3-1	This person is:	US only
III-3-2	Applicant for	
III-3-4	Name (LAST, First)	CHUNG, Kwang Jin
III-3-5	Address:	Bosung Apt. 611-1008, Kwonsun-dong, Kwonsun-gu, Suwon-city, 441-390 Kyungki-do Republic of Korea
III-3-6	State of nationality	KR
III-3-7	State of residence	KR
III-4	Applicant and/or inventor	applicant and inventor
III-4-1	This person is:	US only
III-4-2	Applicant for	
III-4-4	Name (LAST, First)	AN, Byoung Woo
III-4-5	Address:	Hanju Apt. 101-403, Seryu 2-dong, Kwonsun-gu, Suwon-city, 441-112 Kyungki-do Republic of Korea
III-4-6	State of nationality	KR
III-4-7	State of residence	KR
III-5	Applicant and/or inventor	applicant and inventor
III-5-1	This person is:	US only
III-5-2	Applicant for	
III-5-4	Name (LAST, First)	KWON, Oh Yeon
III-5-5	Address:	1-117, Sugi-ri, Bongdam-myeon, Hwasung-gun, 445-890 Kyungki-do Republic of Korea
III-5-6	State of nationality	KR
III-5-7	State of residence	KR

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III-6	Applicant and/or inventor	
III-6-1	This person is:	applicant and inventor
III-6-2	Applicant for	US only
III-6-4	Name (LAST, First)	YOO, Hong Jae
III-6-5	Address:	Dongbu Hannong Chemical Co., Ltd. Company House 303, 175-1, Botong-ri, Jungnam-myeon, Hwasung-gun, 445-960 Kyungki-do Republic of Korea
III-6-6	State of nationality	KR
III-6-7	State of residence	KR
III-7	Applicant and/or inventor	
III-7-1	This person is:	applicant and inventor
III-7-2	Applicant for	US only
III-7-4	Name (LAST, First)	KWON, Yong Woong
III-7-5	Address:	103, Seodun-dong, Kwonsun-gu, Suwon-city, 441-100 Kyungki-do Republic of Korea
III-7-6	State of nationality	KR
III-7-7	State of residence	KR
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	SHIN, Dong Joon
IV-1-2	Address:	Woonam Bldg. 10th Fl., 824-22, Yeoksam-dong, Kangnam-gu 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	02-563-2321
IV-1-4	Facsimile No.	02-563-2320
IV-1-5	e-mail	hangil@korea-patent.com
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	CN JP US

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V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	22 September 1999 (22.09.1999)
VI-1-2	Number	99-41035
VI-1-3	Country	KR 1999
VII-1	International Searching Authority Chosen	Korean Industrial Property Office (KIPO) (ISA/KR)
VIII	Check list	number of sheets electronic file(s) attached
VIII-1	Request	5 -
VIII-2	Description	12 -
VIII-3	Claims	1 -
VIII-4	Abstract	1 opapct146.txt
VIII-5	Drawings	0 -
VIII-7	TOTAL	19
	Accompanying items	paper document(s) attached electronic file(s) attached
VIII-8	Fee calculation sheet	✓ -
VIII-9	Separate signed power of attorney	✓ -
VIII-16	PCT-EASY diskette	- diskette
VIII-18	Figure of the drawings which should accompany the abstract	
VIII-19	Language of filing of the international application	Korean
IX-1	Signature of applicant or agent	
IX-1-1	Name (LAST, First)	SHIN, Dong Joon

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10-1	Date of actual receipt of the purported international application	19 September 2000 (19.09.00)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	

• CORRECTED EX OFFICIO BY RO

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10-5	International Searching Authority	ISA/KR
10-6	Transmittal of search copy delayed until search fee is paid	

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11-1	Date of receipt of the record copy by the International Bureau	10 OCTOBER 2000	(10.10.00)
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파라콰트 입상수화제 조성물 및 그의 제조방법

기술분야

본 발명은 일반적으로 토양에 존재하는 광물질에 강하게 흡착되어 제초활성을 나타내지 못한다고 알려진 비선택성 제초제의 활성성분인 파라콰트 디클로라이드 (이하 "파라콰트"라 한다)의 입상수화제 조성물 및 그의 제조방법에 관한 것으로, 보다 상세하게는 5 내지 50 중량%의 파라콰트, 5 내지 30 중량%의 계면활성제, 1 내지 20 중량%의 붕괴촉진제, 잔량으로서의 증량제를 혼합, 반죽하고 입상 제조기를 통해 성형한 후 건조한 파라콰트 입상수화제 조성물 및 그의 제조방법에 관한 것이다.

배경기술

현재 제품으로 판매중인 파라콰트 24.5% 액제의 경우, 처리시 약액에 의해 피부가 손상을 받고 피부를 통해 흡수 이행할 뿐만 아니라 비산된 약액이 호흡기를 통해 흡수되어 중독될 수 있는 위험이 있었고, 고의 또는 과실에 의해 섭취시, 섭취 후 4시간 이내에 응급조치를 하지 않을 경우 치사하는 경우가 많았다.

또한 파라콰트의 엽면부착력을 증가시키기 위해 음이온성 계면활성제를 첨가할 경우, 파라콰트와 음이온성 계면활성제간의 응집 또는 침전물이 생성되어 이러한 문제점을 지방족 또는 방향족의 킬레이팅 화합물을 사용하여 개선하고자 하는 시도(미국특허 등록번호 : 5668086호)가 있었으나, 이 또한 상기의 안전성 문제를 야기할 수 있는 문제점이 있었다.

이러한 안전상의 문제점을 해결하기 위해 액제 이외의 다른 제형으로 개발하고자 하는 시도가 있었으나 파라콰트는 토양에 존재하는 광물질, 특히 증량제로 사용되고 있는 클레이, 벤토나이트, 탈크, 파이로필라이트, 몬몰릴로나이트 등에 강하게 흡착되어 제초활성을 나타내지 못한다고 알려져 타 제형에 대한 개발이 제한되었다.

이러한 시도의 하나로 분말상의 아미트롤(Amitrole)을 액상의 파라콰트와 혼합하여 수용성 입제로 제조하는 방법(미국특허 등록번호 : 5635445)이 보고되었으나, 이 또한 파라콰트 액제에 비해 약효가 미흡할 뿐만 아니라 두 가지 원제의 합제로 제조함에 따라 원가상승의 요인이 있었다.

또한 수화제로 제조하는 연구가 있었으나, 이 경우에도 처리한 분말이 비산되어 호흡기를 통해 흡수될 수 있는 흡입독성의 문제점 및 수화제로 제조시, 파라콰트

를 정제하여 사용해야 함으로써 원가 상승의 문제점이 있었다.

따라서 이러한 여러 문제점을 해결할 수 있고 제초효과가 뛰어나면서도 값싸고 안전한 제형의 개발이 요구되었다.

발명의 개시

본 발명의 목적은, 토양에 존재하는 광물질, 특히 증량제로 사용되고 있는 클레이, 벤토나이트, 탈크, 파이로필라이트, 몬몰릴로나이트 등에 강하게 흡착되어 제초활성을 나타내지 못한다고 알려진 비선택성 제초제의 활성성분인 파라콰트, 계면활성제, 붕괴촉진제와 증량제를 혼합하여 반죽하고 입상으로 성형한 후 건조하여 입상수화제로 제조함으로써 논둑이나 비농경지의 잡초에 대해 파라콰트 액제 및 수화제에 비해 제초효과가 우수한 입상수화제 및 그의 제조방법을 제공하는데 있다.

본 발명의 또다른 목적은, 농약 활성성분으로서의 파라콰트, 계면활성제, 붕괴촉진제와 증량제를 혼합하여 입상수화제로 제조함으로써 파라콰트 액제나 수화제에 의해 유발될 수 있는 접촉, 흡입에 의한 중독을 줄일 수 있을 뿐만 아니라 고의 또는 과실에 의한 섭취의 위험을 예방할 수 있는 안전한 농약조성물을 제공하는데 있다.

상기 목적을 달성하기 위한 본 발명에 따른 파라콰트 입상수화제는 5 내지 50 중량%의 파라콰트 디클로라이드, 5 내지 30 중량%의 계면활성제, 1 내지 20 중량%의 붕괴촉진제, 잔량으로서의 증량제를 포함하며, 상기 성분들을 혼합한 후 소량의 물과 함께 반죽하고 조립기 등을 사용하여 성형한 후 건조시킨 형태로 이루어진다.

상기 농약활성성분인 파라콰트는 약효발현속도가 빠르고 방제할 수 있는 잡초의 영역이 다양한 우수한 제초 활성물질이다.

상기 계면활성제로는 음이온성 계면활성제, ~~비이온성~~ 비이온성 계면활성제가 사용될 수 있다.

상기 붕괴촉진제로는 황산나트륨(sodium sulfate)(Na_2SO_4), 질산나트륨(sodium nitrate)((NaNO_3), 염화칼륨(potassium chloride)(KCl), 황산암모늄(ammonium sulfate)((NH_4) $_2\text{SO}_4$), 요소(urea), 폴리비닐 피롤리돈(polyvinyl pyrrolidone) 등이 사용될 수 있다.

상기 증량제로서는 다이얼라이트, 카울린, 클레이, 화이트카본, 수용성 전분, 탄

산칼슘(calcium carbonate), 벤토나이트, 파이로필라이트, 탈크 등이 사용될 수 있다.

본 발명에 따른 파라콰트 입상수화제의 제조방법은 1) 상기 농약활성성분으로서의 파라콰트 디클로라이드와 계면활성제, 붕괴촉진제, 잔량으로서의 증량제를 혼합하여 100 중량%로 한 후 0 내지 15 중량%의 물과 함께 10분 내지 1시간 상온에서 반죽하는 반죽단계; 2) 상기 1)의 단계의 생성물을 조립기를 사용하여 입상으로 제조하는 성형단계; 및 3) 상기 2)의 단계의 생성물을 유동층건조기 내 70 내지 150 °C의 온도에서 10분 내지 1시간 동안 건조하는 건조단계;를 포함하여 이루어진다.

최선의 실시예

이하 본 발명의 구체적인 실시예를 참조하여 상세히 설명한다.

본 발명에 따른 파라콰트 입상수화제는 5 내지 50 중량%의 파라콰트 디클로라이드, 5 내지 30 중량%의 계면활성제, 1 내지 20 중량%의 붕괴촉진제, 잔량으로서의 증량제를 포함하며, 상기 성분들을 혼합한 후 소량의 물과 함께 반죽하고 조립기 등을 사용하여 성형한 후 건조시킨 형태로 이루어진다.

상기 파라콰트 디클로라이드는 직접 대상 논둑 및 비농경지의 잡초를 방제하는 역할을 하는 것으로 1,1'-Dimethyl-4,4'-bipyridyldiylum dichloride의 화학명을 가지는 물질로 이해될 수 있다. 이 파라콰트 디클로라이드의 순도는 10 내지 100%가 될 수 있으며, 이는 상용적으로 제공되는 원료의 공급업체에서의 제형에 따라 적절히 선택하여 사용할 수 있음은 당연히 이해될 수 있는 것이다.

상기 계면활성제는 계면활성이 큰 물질로서 분자 중에 친수성 및 친유성 분자단을 가진 양친매성 물질로서, 세정력, 분산력, 유화력, 가용화력, 습윤력, 살균력, 기포력 및 침투력 등이 우수하다는 특징을 갖는 것으로 이해되는 물질이며, 본 발명에 따른 유효성분 파라콰트가 효과적으로 약효를 발현하도록 습윤, 붕괴, 분산시키는 작용을 하는 것으로 이해될 수 있다.

상기 계면활성제로는 알킬(C₈₋₁₂)아릴설포네이트(alkyl(C₈₋₁₂) aryl sulfonate), 디알킬(C₃₋₆)아릴설포네이트, 디알킬(C₈₋₁₂)설포석시네이트(dialkyl(C₈₋₁₂) sulfosuccinate), 리그닌설포네이트(lignin sulfonate), 나프탈렌(naphthalene)설포네이트축합물, 나프탈렌설포네이트포르마린(formalin)축합물, 알킬(C₈₋₁₂)나프탈렌설포네이트포르마린축합물, 폴리옥시에틸렌알킬(C₈₋₁₂)페닐설포네이트와 같은

설포네이트 화합물의 소듐염 또는 칼슘염, 알킬(C_{8-12})설페이트, 알킬(C_{8-12})아릴설페이트, 폴리옥시에틸렌알킬(C_{8-12})설페이트, 폴리옥시에틸렌알킬(C_{8-12})페닐설페이트와 같은 설페이트 화합물의 소듐염 또는 칼슘염, 폴리옥시알킬렌석시네이트(polyoxyalkylene succinate)와 같은 석시네이트화합물의 소듐염 또는 칼슘염, 소듐 벤조에이트(sodium benzoate), 알킬카르복실레이트(alkyl carboxylate) 등의 음이온성 계면활성제, 폴리옥시에틸렌알킬(C_{8-12})에테르, 폴리옥시에틸렌알킬(C_{8-12})페닐에테르, 폴리옥시에틸렌알킬(C_{8-12})페닐폴리머 에틸렌옥사이드 프로필렌옥사이드 코폴리머와 같은 비이온성 계면활성제가 단독으로 또는 2종 이상 혼합되어 사용될 수 있으며, 이들은 모두 예시적으로 열거한 것들로서, 이들 이외의 다른 계면활성제들도 사용될 수 있음은 당해 기술분야에서 통상의 지식을 갖춘 자에게는 용이하게 이해될 수 있을 것이다.

상기 붕괴촉진제는 본 발명에 따른 파라콰트 입상수화제의 붕괴, 분산작용을 촉진시키는 역할을 하는 물질로서 황산나트륨(Na_2SO_4), 질산나트륨($NaNO_3$), 염화칼륨(KCl), 황산암모늄($(NH_4)_2SO_4$), 요소, 폴리비닐 피롤리돈 등이 사용될 수 있다.

상기 증량제는 본 발명에 따른 농약조성물의 충전제의 역할을 하는 것으로 농약조성물의 형태를 유지할 수 있을 뿐만 아니라 바라는 농약 활성성분의 효과 발현에 보조적인 작용을 하는 물질로서 다이알라이트, 카울린, 클레이, 화이트카본, 수용성 전분, 탄산칼슘, 벤토나이트, 파이로필라이트, 탈크 등이 사용될 수 있으며 이외의 증량제 들도 사용될 수 있음은 당해 기술분야에서 통상의 지식을 갖춘 자에게는 용이하게 이해될 수 있을 것이다.

이하 본 발명에 따른 파라콰트 입상수화제의 바람직한 실시예 및 비교예들이 기술되어질 것이다. 이하의 실시예들은 본 발명을 예증하기 위한 것으로 본 발명의 범위를 국한시키는 것으로 이해되어져서는 안될 것이다.

실시예1

원제 함량 42.5%인 파라콰트 원제 30 중량%, 소듐 나프탈렌설포네이트 포름알데히드 축합물 5 중량%, 에틸렌옥사이드 프로필렌옥사이드 코폴리머 2 중량%, 옥틸 나프탈렌설포네이트 5 중량%, 황산암모늄 5 중량%, 잔량으로서의 파이로필라이트를 혼합하여 100 중량%로 한 후, 상기 혼합물 대비 8 중량%의 물을 넣고 반죽하여 조립기를 통해 성형하고 흡기 $120^{\circ}C$ 의 유동층 건조기내에서 30분간 건조하여 제조한 파라콰트 입상수화제를 생물시험 및 이화학적 분석에 사용하였다.

실시예2

원제 함량 42.5%인 파라콰트 원제 30 중량%, 소듐 옥틸나프탈렌설포네이트 5 중량%, 에틸렌옥사이드 프로필렌옥사이드 코폴리머 2 중량%, 옥틸벤젠설페이트 5 중량%, 질산나트륨 5 중량%, 잔량으로서의 파이로필라이트를 혼합하여 100 중량%로 한 후, 상기 혼합물 대비 8 중량%의 물을 넣고 반죽하여 조립기를 통해 성형하고 흡기 120℃의 유동층 건조기내에서 30분간 건조하여 제조한 파라콰트 입상수화제를 생물시험 및 이화학적 분석에 사용하였다.

실시예3

원제 함량 42.5%인 파라콰트 원제 40 중량%, 소듐 나프탈렌설포네이트 포름알데히드 축합물 5 중량%, 에틸렌옥사이드 프로필렌옥사이드 코폴리머 2 중량%, 옥틸나프탈렌설포네이트 5 중량%, 황산암모늄 5 중량%, 잔량으로서의 파이로필라이트를 혼합하여 100 중량%로 한 후, 상기 혼합물 대비 8 중량%의 물을 넣고 반죽하여 조립기를 통해 성형하고 흡기 120℃의 유동층 건조기내에서 30분간 건조하여 제조한 파라콰트 입상수화제를 생물시험 및 이화학적 분석에 사용하였다.

실시예4

원제 함량 42.5%인 파라콰트 원제 40 중량%, 소듐 옥틸나프탈렌설포네이트 5 중량%, 에틸렌옥사이드 프로필렌옥사이드 코폴리머 2 중량%, 옥틸벤젠설페이트 5 중량%, 질산나트륨 5 중량%, 잔량으로서의 파이로필라이트를 혼합하여 100 중량%로 한 후, 상기 혼합물 대비 8 중량%의 물을 넣고 반죽하여 조립기를 통해 성형하고 흡기 120℃의 유동층 건조기내에서 30분간 건조하여 제조한 파라콰트 입상수화제를 생물시험 및 이화학적 분석에 사용하였다.

비교예1

본 발명에 따라 제조한 각 실시예의 입상수화제와 비교하기 위해 현재 시판되고 있는 파라콰트 24.5% 액제를 구입하여 생물시험에 사용하였다.

비교예2

본 발명에 따라 제조한 각 실시예의 입상수화제와 비교하기 위해 현재 시판되고

있는 글라이포세이트 이소프로필아민 41% 액제를 구입하여 생물시험에 사용하였다.

피에 대한 약효 확인시험

각 실시예에 따라 제조한 시제품 및 비교예1 및 비교예2의 제품을 약제처리후 1일, 2일, 4일, 7일, 10일, 14일에 걸쳐 피에 대한 약효를 확인하였다.

초장이 42cm인 피에 대해 표1과 같이 처리하여 약효를 조사하였다.

【표 1】 피에 대한 약효 확인시험 결과

구 분	처리량 (/10a)	처리후 약효(%)					
		1일	2일	4일	7일	10일	14일
실시예1	580g	90	95	95	90	85	70
	1160g	96	98	97	94	90	90
실시예2	580g	90	93	94	88	80	73
	1160g	95	96	97	93	88	85
실시예3	435g	93	94	96	90	80	75
	870g	96	98	98	94	92	88
실시예4	435g	92	95	93	90	80	78
	870g	96	96	96	92	90	88
비교예1	300ml	90	94	94	90	77	60
	600ml	95	96	95	88	80	60
비교예2	300ml	5	10	20	70	82	93
	600ml	10	20	30	85	88	97

상기 시험결과와 같이 각 실시예에 따라 제조한 파라콰트 입상수화제는 기준량, 배량 처리시 비교예1의 파라콰트 액제에 비해 피에 대해 우수한 약효를 보였으며, 5일 이후 피가 재생되는 비율도 적어 약효 지속력에서도 우수한 효과를 나타내었으며, 비교예2의 글라이포세이트 액제에 비해서도 초기 약효에서 매우 우수한 약효를 나타내었다.

바랭이에 대한 약효 확인시험

각 실시예에 따라 제조한 시제품 및 비교예1 및 비교예2의 제품을 약제처리후 1일, 2일, 4일, 7일, 10일, 14일에 걸쳐 바랭이에 대한 약효를 확인하였다.

초장이 45cm인 바랭이에 대해 표2와 같이 처리하여 약효를 조사하였다.

【표 2】바랭이에 대한 약효 확인시험 결과

구 분	처리량 (/10a)	처리후 약효(%)					
		1일	2일	4일	7일	10일	14일
실시예1	580g	94	98	99	98	88	74
	1160g	96	98	99	99	96	90
실시예2	580g	95	97	98	98	90	73
	1160g	98	98	99	99	98	95
실시예3	435g	96	98	98	99	93	85
	870g	97	98	98	98	92	88
실시예4	435g	94	97	98	96	90	78
	870g	96	99	99	99	97	88
비교예1	300ml	94	96	95	93	87	70
	600ml	95	97	97	96	90	80
비교예2	300ml	10	20	40	75	92	95
	600ml	15	30	50	85	93	99

상기 시험결과와 같이 각 실시예에 따라 제조한 파라콰트 입상수화제는 기준량, 배량 처리시 비교예1의 파라콰트 액제에 비해 바랭이에 대해 우수한 약효를 보였으며, 약효 지속력도 우수하였으며, 초기 방제가에서도 94% 이상으로 아주 우수한 효과를 나타내었다.

망초에 대한 약효 확인시험

각 실시예에 따라 제조한 시제품 및 비교예1 및 비교예2의 제품을 약제처리후 1일, 2일, 4일, 7일, 10일, 14일에 걸쳐 망초에 대한 약효를 확인하였다.

초장이 12cm인 망초에 대해 표3과 같이 처리하여 약효를 조사하였다.

【표 3】 망초에 대한 약효 확인시험 결과

구 분	처리량 (/10a)	처리후 약효(%)					
		1일	2일	4일	7일	10일	14일
실시예1	580g	85	88	90	85	80	70
	1160g	86	88	92	90	85	77
실시예2	580g	80	88	88	88	78	68
	1160g	85	90	92	88	84	75
실시예3	435g	85	90	90	90	85	70
	870g	90	92	93	94	92	80
실시예4	435g	85	89	89	90	86	72
	870g	90	90	90	89	85	80
비교예1	300ml	80	86	85	85	76	65
	600ml	90	90	89	88	88	70
비교예2	300ml	10	20	30	40	70	73
	600ml	10	25	45	60	82	83

상기 시험결과와 같이 각 실시예에 따라 제조한 파라콰트 입상수화제는 기준량, 배량 처리시 비교예1의 파라콰트 액제에 비해 망초에 대해 우수한 약효를 보였으며, 망초의 재생율도 비교예1의 약제에 비해 적어 우수한 약효지속효과를 나타내었으며, 각 실시예에 따라 제조한 약제는 초기 약효에서도 비교예의 약제에 비해 매우 우수한 약효를 나타내었다.

쑥에 대한 약효 확인시험

각 실시예에 따라 제조한 시제품 및 비교예1 및 비교예2의 제품을 약제처리후 1일, 2일, 4일, 7일, 10일, 14일에 걸쳐 쑥에 대한 약효를 확인하였다.

초장이 20cm인 쑥에 대해 표4와 같이 처리하여 약효를 조사하였다.

【표 4】쑥에 대한 약효 확인시험 결과

구 분	처리량 (/10a)	처리후 약효(%)					
		1일	2일	4일	7일	10일	14일
실시예1	580g	86	95	96	92	87	80
	1160g	90	98	100	95	90	85
실시예2	580g	85	93	97	93	88	83
	1160g	88	96	99	94	90	86
실시예3	435g	86	96	96	90	85	80
	870g	90	98	100	96	91	86
실시예4	435g	86	93	96	91	86	81
	870g	88	96	100	95	90	85
비교예1	300ml	85	90	93	89	84	76
	600ml	88	92	95	90	85	80
비교예2	300ml	5	5	20	40	70	92
	600ml	5	10	25	60	85	99

상기 시험결과와 같이 각 실시예에 따라 제조한 파라콰트 입상수화제는 기준량, 배량 처리시 비교예1의 파라콰트 액제에 비해 쑥에 대해 우수한 약효를 보였으며, 14일차 약효조사에서도 쑥의 재생율이 파라콰트 액제에 비해 매우 낮아 우수한 약효 지속효과를 나타내었다.

깨풀에 대한 약효 확인시험

각 실시예에 따라 제조한 시제품 및 비교예1 및 비교예2의 제품을 약제처리후 1일, 2일, 4일, 7일, 10일, 14일에 걸쳐 깨풀에 대한 약효를 확인하였다.

초장이 15cm인 깨풀에 대해 표5와 같이 처리하여 약효를 조사하였다.

【표 5】 깨풀에 대한 약효 확인시험 결과

구 분	처리량 (/10a)	처리후 약효(%)					
		1일	2일	4일	7일	10일	14일
실시예1	580g	80	90	95	100	100	98
	1160g	86	94	100	100	100	99
실시예2	580g	82	93	95	99	100	97
	1160g	85	96	97	100	100	100
실시예3	435g	83	89	96	100	100	96
	870g	86	98	100	100	100	99
실시예4	435g	82	90	95	100	100	97
	870g	86	96	96	100	100	100
비교예1	300ml	80	90	96	100	100	95
	600ml	85	96	98	100	100	97
비교예2	300ml	0	0	8	20	30	40
	600ml	0	0	10	25	40	50

상기 시험결과와 같이 각 실시예에 따라 제조한 파라콰트 입상수화제는 기준량, 배량 처리시 비교예1의 파라콰트 액제에 비해 깨풀에 대해 우수한 방제효과를 나타내었으며, 약효조사 14일차에도 재생되는 깨풀은 거의 없었다.

장기 보관시 약효 안정성 확인시험

장기 보관에 따른 파라콰트 입상수화제의 약효저하여부를 점검하기 위해 일정 기간동안 보관중인 시료를 피에 대해 약효시험을 수행하였다.

각 실시예에 따라 제조한 시제품 및 비교예1의 제품을 제제직후, 1개월, 2개월, 3개월, 6개월, 1년간 보관후 보관중인 약제를 표6과 같이 처리한 후 다음날 1일차 약효조사를 수행하였다.

【표 6】 장기보관후 약효 확인시험 결과

구 분	처리량 (/10a)	장기보관후 채취시료의 약효(%)				
		제제직후 시료	1개월차 시료	2개월차 시료	6개월차 시료	1년차 시료
실시예1	580g	90	92	88	91	89
실시예2	580g	91	90	89	91	92
실시예3	435g	89	88	90	98	91
실시예4	435g	92	87	90	90	88
비교예1	300ml	89	90	91	90	87

상기 표6과 같이 상기 실시예와 같이 제조한 파라콰트 입상수화제는 장기보관후에도 피에 대한 약효에서 비교예의 약제와 같이 우수한 약효를 발현하여 장기저장시에도 약효발현에 문제없는 제조방법을 제공하는 효과가 있었다.

저장 안정성 시험

각 실시예에 따라 제조한 시제품의 저장안정성을 확인하기 위하여 15℃, 50℃에서의 경시변화시험을 수행하였다.

【표 7】 파라콰트 입상수화제의 저장안정성 시험결과

구 분	저장온도	원제함량(%)					
		제제직후	2주	4주	8주	16주	32주
실시예1	15℃	12.8	12.8	12.8	12.8	12.8	12.8
	50℃	12.8	12.8	12.8	12.7	12.7	12.6
실시예2	15℃	12.8	12.8	12.8	12.8	12.8	12.8
	50℃	12.8	12.8	12.8	12.8	12.7	12.7
실시예3	15℃	17.0	17.0	17.0	17.0	17.0	17.0
	50℃	17.0	16.9	16.9	16.9	16.9	16.7
실시예4	15℃	17.0	17.0	17.0	17.0	17.0	17.0
	50℃	17.0	17.0	17.0	16.9	16.8	16.8

상기 시험결과와 같이 본 발명에 따라 제조한 파라콰트 입상수화제는 50℃ 학대경변시험결과에서 32주 보관시에도 2% 미만의 원제만이 분해되어 장기 보관시에도 안정된 조성물을 제공하는 효과가 있었다.

이상의 시험결과와 같이 본 발명에 따른 파라콰트 입상수화제는 피, 바랭이, 망초, 쑥, 깨풀에 대해 약효가 우수할 뿐만 아니라 피, 바랭이, 망초와 같이 재생력이 뛰어난 잡초에 대해서도 잡초 재생율이 낮은 조성물을 제공하는 효과가 있었으며, 장기저장시에도 피에 대한 약효 및 유효성분 안정성에도 문제가 없는 조성물을 제공할 수 있었다.

산업상 이용 가능성

따라서, 본 발명에 의하면 일반적으로 토양에 존재하는 광물질, 특히 증량제로 사용되고 있는 클레이, 벤토나이트, 탈크, 파이로필라이트, 몬몰릴로나이트 등에 강하게 흡착되어 제초활성을 나타내지 못한다고 알려진 비선택성 제초제의 활성 성분인 파라콰트 디클로라이드와 증량제를 혼합, 반죽하고 성형한 후 건조하여 제조한 파라콰트 입상수화제 및 그의 제조방법에 관한 것으로 본 발명에 따라 입상수화제로 제조함으로써 기존의 액제 및 수화제의 취급 및 사용시 발생할 수 있는 접촉 또는 흡입에 의한 중독의 위험성을 방지할 수 있을 뿐만 아니라 고의 또는 과실에 의한 약제 섭취에 따른 약제중독의 가능성을 제거한 조성물을 제공하는 효과가 있다.

또한 본 발명에 따라 파라콰트 입상수화제를 제조하더라도, 장기 보관 후 약제의 효과가 유지되어 논둑이나 비농경지의 잡초를 효과적으로 방제할 수 있을 뿐만 아니라 파라콰트 액제의 특성인 속효성을 유지하여 처리후 3일 만에 잡초를 고사시킬 수 있는 조성물을 제공하는 효과가 있다.

이상에서 본 발명은 기재된 구체예에 대해서만 상세히 설명되었지만 본 발명의 기술사상 범위 내에서 다양한 변형 및 수정이 가능함은 당업자에게 있어서 명백한 것이며, 이러한 변형 및 수정이 첨부된 특허청구범위에 속함은 당연한 것이다.

특허청구범위**【청구항 1】**

5 내지 50 중량%의 파라콰트 디클로라이드, 5 내지 30 중량%의 계면활성제, 1 내지 20 중량%의 붕괴촉진제, 잔량으로서의 증량제를 포함하며, 상기 성분들을 혼합한 후 소량의 물과 함께 반죽하고 조립기 등을 사용하여 성형한 후 건조시킨 형태로 이루어짐을 특징으로 하는 파라콰트 입상수화제.

【청구항 2】

제 1 항에 있어서,

상기 계면활성제로는 음이온성 계면활성제, 비이온성 계면활성제가 사용됨을 특징으로 하는 파라콰트 입상수화제.

【청구항 3】

제 1 항에 있어서,

상기 붕괴촉진제로는 황산나트륨, 질산나트륨, 염화칼륨, 황산암모늄, 요소, 폴리비닐 피롤리돈 등이 사용됨을 특징으로 하는 파라콰트 입상수화제.

【청구항 4】

제 1 항에 있어서,

상기 증량제로서는 다이얼라이트, 카올린, 클레이, 화이트카본, 수용성 전분, 탄산칼슘, 벤토나이트, 파이로필라이트, 탈크 등이 사용됨을 특징으로 하는 파라콰트 입상수화제.

【청구항 5】

1) 상기 파라콰트와 잔량으로서의 증량제를 혼합하여 이 혼합물 대비 1 내지 15 중량%의 물과 함께 10분 내지 1시간 동안 상온에서 반죽하는 반죽단계;

2) 상기 1)의 단계의 생성물을 조립기를 사용하여 입상으로 제조하는 성형단계; 및

3) 상기 2)의 단계의 생성물을 유동층건조기내 70 내지 150℃의 온도에서 10분 내지 1시간 동안 건조하는 건조단계;

를 포함하여 이루어짐을 특징으로 하는 파라콰트 입상수화제의 제조방법.

요약서

본 발명은 일반적으로 토양에 존재하는 광물질, 특히 증량제로 사용되고 있는 클레이, 벤토나이트, 탈크, 파이로필라이트, 몬몰릴로나이트 등에 강하게 흡착되어 제초활성을 나타내지 못한다고 알려진 비선택성 제초제의 활성성분인 파라콰트 디클로라이드(이하 "파라콰트")를 입상수화제의 형태로 제제함으로써 약제의 안전성을 증진시킬 수 있을 뿐만 아니라 액제, 수화제 등 다른 제형에 비해 약효가 우수한 파라콰트 입상수화제 조성물 및 그의 제조방법에 관한 것이다.

본 발명에 따른 농약 조성물은 5 내지 50 중량%의 파라콰트, 5 내지 30 중량%의 계면활성제, 1 내지 20 중량%의 붕괴촉진제, 잔량으로서의 증량제를 혼합하고 반죽하여 입상수화제로 성형한 후 건조하여 이루어진다.

따라서 본 발명에 의해 피부독성, 흡입독성의 문제를 야기할 수 있는 파라콰트를 입상수화제로 제제함으로써 농약 처리시에 접촉에 의한 피부손상, 호흡기를 통한 호흡기 손상을 방지할 수 있을 뿐만 아니라 고의 또는 과실에 의한 농약 섭취의 가능성을 미연에 예방할 수 있는 조성물을 제공하는 효과가 있다.

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(54) Title: WATER DISPERSIBLE GRANULE CONTAINING PARAQUAT DICHLORIDE AND ITS PREPARING METHOD

(57) Abstract: The present invention relates to a water dispersible granule containing Paraquat Dichloride and preparation method thereof. The paraquat, an active component of a nonselective herbicide, is generally known to be inactive due to its strong adsorption to minerals in the soil, particularly to extender such as clay, bentonite, talc, pyrophyllite, montmorillonite, etc. Paraquat is transformed into the water dispersible granule type, so that the dispersible granule type can have safety to human body and superior agrichemical effect than other formulation types such as soluble concentrate type or wettable powder type. The agrichemical composition according to the present invention is prepared by mixing and kneading 5-50 wt.% of paraquat, 5-30 wt.% of surfactant, 1-2 wt.% of disintegrant and the rest of carrier, forming granules out of kneaded mixture, and drying the granules.

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WATER DISPERSIBLE GRANULE CONTAINING PARAQUAT DICHLORIDE AND ITS PREPARING METHOD

Technical Field

5 The present invention relates to a water dispersible granule containing Paraquat Dichloride (hereunder referred to as "Paraquat") and its preparing method. Paraquat, an active component of a nonselective herbicide, is generally known not to show herbicidal activity since it is strongly adsorbed to minerals in the soil. More particularly, the invention relates to a water dispersible granule containing Paraquat and its preparing
10 method that comprises mixing and kneading 5-50wt% of Paraquat, 5-30wt% of surfactant, 1-20wt% of breakage promoter and the rest of extender, forming granules out of kneaded mixture using a granulator, and drying the granules.

Background Art

15 Soluble concentrate of 24.5%-Paraquat, currently sold in the market may cause skin damage and may be absorbed through skin when it comes in contact with skin. The soluble concentrate sprayed may be inhaled through the respiratory organ to cause poisoning. Further, it can be fatal to ingest it by accident or on purpose unless first aid is taken within 4 hours after ingestion.

20 In case anionic surfactant is added to increase adhesion between leaf and Paraquat, there may be problem of cohesion or precipitation between Paraquat and anionic surfactant. There was an attempt to solve this problem using aliphatic or aromatic chelating compound (US Patent No. 5668086). However, it could not solve aforementioned safety problem.

To solve the safety problem, there was an attempt to prepare Paraquat composition having a formulation type other than soluble concentrate type. However, the attempt was limited since Paraquat is known to be adsorbed tightly to minerals, especially to the ones used as extenders such as clay, bentonite, talc, pyrophyllite and montmorillonite, and consequently show no herbicidal activity.

As another attempt, a method of preparing a water soluble granule by mixing powdery amitrole with liquid Paraquat was reported (US Patent No. 5635445). However, the water soluble granule provides weaker effect than the soluble concentrate, and cost is increased because it is prepared with two components.

Further, there was an attempt to prepare the paraquat composition as a wettable powder, which has problems of inhalation poisoning of the scattered powder and cost increase related to the purification of Paraquat.

Accordingly, it is required to prepare a formulation type which solves aforementioned problems and has superior herbicidal effect, safety and low cost.

Disclosure of Invention

An object of the present invention is to provide water dispersible granule and its preparing method which comprises mixing and kneading Paraquat, surfactant, breakage promoter, and extender; forming granules out of kneaded mixture; and drying the granules. In this case, Paraquat is, an active component of nonselective herbicide, is known not to show herbicidal activity due to its strong adsorption to minerals in the soil, particularly to the ones used as extenders such as clay, bentonite, talc, pyrophyllite and montmorillonite. Further, the water dispersible granule shows a superior herbicidal effect on weeds on ridgeway or non-farm land, compared with the soluble concentrate or

the wettable powder of Paraquat.

Another object of the present invention is to provide a safe agrichemical composition which reduces poisoning caused by contact or ingestion and prevents the danger of intake by accident or on purpose, by mixing Paraquat (active component of the agrichemical), surfactant, breakage promoter and extender, and forming granules out of mixture.

To achieve the object of the invention, water dispersible granule containing paraquat according to the present invention comprises 5-50wt% of Paraquat, 5-30wt% of surfactant, 1-20wt% of breakage promoter and the rest of extender, wherein said water dispersible granule is prepared by mixing the above components, kneading mixture together with a small amount of water, forming granules out of kneaded mixture using a granulator or the like and drying the granules.

Paraquat, an agrichemical active component, is a superior herbicidal active compound, which shows fast effect and removes various weeds.

As the surfactant, anionic surfactant and/or nonionic surfactant can be used.

As the breakage promoter, at least one selected from the group consisting of sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3), potassium chloride (KCl), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), urea, polyvinyl pyrrolidone and the like can be used.

As the extender, at least one selected from the group consisting of diollite, kaolin, clay, white carbon, watersoluble starch, calcium carbonate, bentonite, pyrophyllite, talc and the like can be used.

A preparing method of water dispersible granule containing paraquat according to the present invention comprises: a) mixing paraquat dichloride, surfactant, breakage promoter and extender, and kneading mixture together with 1-15wt% of water for the

mixture at room temperature for 10min-1hr; b) forming granules out of product of step a) using a granulator; and c) drying product of step b) in a fluidized bed dryer at 70-150°C for 10min-1hr.

5 Best Mode for Carrying Out the Invention

Water dispersible granule containing paraquat according to the present invention comprises 5-50wt% of Paraquat, 5-30wt% of surfactant, 1-20wt% of breakage promoter and the rest of extender, wherein said water dispersible granule is prepared by mixing the above components, kneading mixture together with a small amount of water, forming granules out of kneaded mixture using a granulator or the like and drying the granules.

The Paraquat removes weeds on ridgeway or non-farm land directly and has the chemical name of 1,1'-dimethyl-4,4'-bipyridylium dichloride. The purity of paraquat may be in the range of 1-100%, and can be selected adequately according to suppliers of paraquat or formulation types.

The surfactant is compound having large surface activity and amphiphilic compound which has both hydrophilic and lipophilic groups in molecule thereof. It is characterized by its superior detergent power, dispersion power, emulsification power, solubilization power, wetting power, germicidal power, bubbling power and infiltration power. It acts as wetting, breakage and dispersion compound such that paraquat can show its activity effectively.

As the surfactant, there can be used at least one selected from the group consisting of sodium or calcium salts of sulfonate such as alkyl (C_{8-12}) arylsulfonate, dialkyl (C_{3-6}) arylsulfonate, dialkyl (C_{8-12}) arylsulfosuccinate, ligninsulfonate, naphthalenesulfonate

condensate, naphthalenesulfonate formalin condensate, alkyl (C₈₋₁₂) naphthalenesulfonate formalin condensate and polyoxyethylenealkyl (C₈₋₁₂) phenylsulfonate; sodium or calcium salts of sulfate such as alkyl (C₈₋₁₂) sulfate, alkyl (C₈₋₁₂) arylsulfate, polyoxyethylenealkyl (C₈₋₁₂) sulfate and polyoxyethylene alkyl (C₈₋₁₂) phenylsulfate; sodium or calcium salts of succinates such as polyoxyalkylenesuccinate; anionic surfactant such as sodium benzoate and alkylcarboxylate; and nonionic surfactant such as polyoxyethelenealkyl (C₈₋₁₂) ether, polyoxyethelenealkyl (C₈₋₁₂) phenylether, polyoxyethelenealkyl (C₈₋₁₂) phenyl polymer and ethylene oxide propylene oxide copolymer. The above compounds are only examples and it may be easily understood to the one in the art that the other surfactants can also be used.

The breakage promoter facilitates breakage and dispersion of the water dispersible granule containing paraquat according to the present invention. There can be used as the breakage promoter at least one selected from the group consisting of Sodium sulfate (Na₂SO₄), sodium nitrate (NaNO₃), potassium chloride (KCl), ammonium sulfate ((NH₄)₂SO₄), urea, polyvinyl pyrrolidone and the like.

The extender works as filler of the water dispersible granule according to the present invention. It maintains the shape of the water dispersible granule and supports the effect development of the agrichemical active component. There can be used as the extender at least one selected from the group consisting of Diollite, kaolin, clay, white carbon, water-soluble starch, bentonite, pyrophyllite, talc and the like. It may be easily understood to the one in the art that the other extenders can also be used.

Hereunder is given detailed description of the water dispersible granule according to the present invention using examples and comparative examples. The following examples are intended to be illustrative of the present invention and should not be

construed as limiting the scope of the present invention.

Example 1

30wt% of 42.5%-Paraquat, 5wt% of sodium naphthalenesulfonate formaldehyde
5 condensate, 2wt% of ethylene oxide propylene oxide copolymer, 5wt% of
octylnaphthalenesulfonate, 5wt% of ammonium sulfate and the rest of pyrophyllite were
mixed. Then, the mixture was kneaded together with 8wt% of water for the mixture at
room temperature for 30 minutes. Next, granules were formed out of kneaded mixture
using a granulator. Then, the granules were dried in a fluidized bed dryer at 120°C of
10 suction air for 30 minutes. Thus prepared water dispersible granules was used for biotest
and physicochemical analysis.

Example 2

30wt% of 42.5%-Paraquat, 5wt% of sodium octylnaphthalenesulfonate, 2wt% of
15 ethylene oxide propylene oxide copolymer, 5wt% of octybenzenesulfate, 5wt% of
sodium nitrate and the rest of pyrophyllite were mixed. Hereinafter, the procedure of
Example 1 was followed.

Example 3

20 40wt% of 42.5%-Paraquat, 5wt% of sodium naphthalenesulfonate formaldehyde
condensate, 2wt% of ethylene oxide propylene oxide copolymer, 5wt% of
octylnaphthalenesulfonate, 5wt% of ammonium sulfate and the rest of pyrophyllite were
mixed. Hereinafter, the procedure of Example 1 was followed.

Example 4

40wt% of 42.5%-Paraquat, 5wt% of sodium octylnaphthalenesulfonate, 2wt% of ethylene oxide propylene oxide copolymer, 5wt% of octybenzenesulfate, 5wt% of sodium nitrate and the rest of pyrophillite were mixed. Hereinafter, the procedure of
5 Example 1 was followed.

Comparative Example 1

Soluble concentrate of 24.5%-Paraquat solution commercially available was purchased and used for biotest in order to compare with the examples of the present
10 invention.

Comparative Example 2

Soluble concentrate of 41%-glyphosate isopropylamine was purchased and used for biotest in order to the comparison with the examples of the present invention.
15

Test of Agrichemical Effect on Barnyard Millet

After treating the barnyard millet with the products prepared from the examples and the comparative examples, the agrichemical effect was checked 1, 2, 4, 7, 10 and 14 days respectively after treatment.

20 The barnyard millet having the length of 42cm was treated according to the results are also disclosed in the following Table 1.

Table 1. Test Result for Barnyard Millet

	Dosage (/10a)	Agrichemical Effect after Treatment(%)					
		1	2	4	7	10	14
		Day	Day	Day	Day	Day	Day
Example 1	580g	90	95	95	90	85	70
	1160g	96	98	97	94	90	90
Example 2	580g	90	93	94	88	80	73
	1160g	95	96	97	93	88	85
Example 3	435g	93	94	96	90	80	75
	870g	96	98	98	94	92	88
Example 4	435g	92	95	93	90	80	78
	870g	96	96	96	92	90	88
Comparative	300ml	90	94	94	90	77	60
Example 1	600ml	95	96	95	88	80	60
Comparative	300ml	5	10	20	70	82	93
Example 2	600ml	10	20	30	85	88	97

As is shown above, the water dispersible granule prepared according to each example showed superior agrichemical effect against barnyard millets, compared with the soluble concentrate of paraquat in comparative example 1 in treatment with reference and double quantity. It also showed superior effect-continuation, that is, lower regenerating ratio after 5 days, and showed much superior initial effect, compared with the soluble concentrate of glyphosate in comparative example 2.

10 Test of Agrichemical Effect on Crab grass

After treating the crab grasses with the products prepared from the examples and the comparative examples, the agrichemical effect was checked 1, 2, 4, 7, 10 and 14 days respectively after treatment.

The crab grasses having the length of 45cm was treated according to the results are also disclosed in the following Table 2.

Table 2. Test Result for Crab Grass

	Dosage (/10a)	Agrichemical Effect after Treatment (%)					
		1	2	4	7	10	14
		Day	Day	Day	Day	Day	Day
Example 1	580g	94	98	99	98	88	74
	1160g	96	98	99	99	96	90
Example 2	580g	95	97	98	98	90	73
	1160g	98	98	99	99	98	95
Example 3	435g	96	98	98	99	93	85
	870g	97	98	98	98	92	88
Example 4	435g	94	97	98	96	90	78
	870g	96	99	99	99	97	88
Comparative Example 1	300ml	94	96	95	93	87	70
	600ml	95	97	97	96	90	80
Comparative Example 2	300ml	10	20	40	75	92	95
	600ml	15	30	50	85	93	99

5

As is shown above, the water dispersible granule prepared according to each example showed superior agrichemical effect against crab grass, compared with the soluble concentrate of paraquat in comparative example 1 in treatment with reference and double quantity. It also showed superior effect-continuation, and showed much superior initial effect(94% or more).

10

Test of Agrichemical Effect on Fleabane

After treating the fleabanes with the products prepared from the examples and the

comparative examples, the agrichemical effect was checked 1, 2, 4, 7, 10 and 14 days respectively after treatment.

The fleabanes having the length of 12cm was treated according to the results are also disclosed in the following Table 3.

5

Table 3. Test Result for Fleabane

	Dosage (/10a)	Agrichemical Effect after Treatment (%)					
		1 Day	2 Day	4 Day	7 Day	10 Day	14 Day
Example 1	580g	85	88	90	85	80	70
	1160g	86	88	92	90	85	77
Example 2	580g	80	88	88	88	78	68
	1160g	85	90	92	88	84	75
Example 3	435g	85	90	90	90	85	70
	870g	90	92	93	94	92	80
Example 4	435g	85	89	89	90	86	72
	870g	90	90	90	89	85	80
Comparative Example 1	300ml	80	86	85	85	76	65
	600ml	90	90	89	88	88	70
Comparative Example 2	300ml	10	20	30	40	70	73
	600ml	10	25	45	60	82	83

As is shown above, the water dispersible granule prepared according to each example showed superior agrichemical effect against fleabanes, compared with the soluble concentrate of paraquat in comparative example 1 in treatment with reference and double quantity. It also showed superior effect-continuation, that is, lower regenerating ratio, compared with agrichemical in the comparative example 1. It also showed much superior initial effect, compared with agrichemical in the comparative

examples.

Test of Agrichemical Effect on Mugwort

After treating the mugworts with the products prepared from the examples and the comparative examples, the agrichemical effect was checked 1, 2, 4, 7, 10 and 14 days respectively after treatment.

The barnyard millet having the length of 20cm was treated according to the results are also disclosed in the following Table 4.

10 Table 4. Test Result for Mugwort

	Dosage (/10a)	Agrichemical Effect after Treatment (%)					
		1 Day	2 Day	4 Day	7 Day	10 Day	14 Day
Example 1	580g	86	95	96	92	87	80
	1160g	90	98	100	95	90	85
Example 2	580g	85	93	97	93	88	83
	1160g	88	96	99	94	90	86
Example 3	435g	86	96	96	90	85	80
	870g	90	98	100	96	91	86
Example 4	435g	86	93	96	91	86	81
	870g	88	96	100	95	90	85
Comparative Example 1	300ml	85	90	93	89	84	76
	600ml	88	92	95	90	85	80
Comparative Example 2	300ml	5	5	20	40	70	92
	600ml	5	10	25	60	85	99

As is shown above, the water dispersible granule prepared according to each example showed superior agrichemical effect against mugworts, compared with the

soluble concentrate of paraquat in comparative example 1 in treatment with reference and double quantity. It also showed superior effect-continuation, that is, lower regeneration ratio after 14 days, compared with the soluble concentrate of paraquat.

5 Test of Agrichemical Effect on Copperleaf

After treating the copperleaves with the products prepared from the examples and the comparative examples, the agrichemical effect was checked 1, 2, 4, 7, 10 and 14 days respectively after treatment.

The copperleaves having the length of 15cm was treated according to the results are also disclosed in the following Table 5.

Table 5. Test Result for Copperleaf

	Dosage (/10a)	Agrichemical Effect after Treatment (%)					
		1 Day	2 Day	4 Day	7 Day	10 Day	14 Day
Example 1	580g	80	90	95	100	100	98
	1160g	86	94	100	100	100	99
Example 2	580g	82	93	95	99	100	97
	1160g	85	96	97	100	100	100
Example 3	435g	83	89	96	100	100	96
	870g	86	98	100	100	100	99
Example 4	435g	82	90	95	100	100	97
	870g	86	96	96	100	100	100
Comparative Example 1	300ml	80	90	96	100	100	95
	600ml	85	96	98	100	100	97
Comparative Example 2	300ml	0	0	8	20	30	40
	600ml	0	0	10	25	40	50

As is shown above, the water dispersible granule prepared according to each example showed superior agrichemical effect against copperleaves, compared with the soluble concentrate of paraquat in comparative example 1 in treatment with reference and double quantity. Further, there were few regenerated copperleaves even 14 days after treatment.

Test of Agrichemical Effect Stability after Long-term Storage

Agrichemical effect of the water dispersible granule that was stored for a predetermined period on barnyard millets was tested in order to check the effect drop.

The products prepared according to the examples and the comparative example 1 were tested immediately after preparation, after 1, 2, 3, 6 and 12 month storage, respectively. The agrichemical effect was checked on the next day of treatment according to the following Table 6.

Table 6. Test Result after Long-term Storage

	Dosage (/10a)	Agrichemical Effect after Treatment (%)				
		Immediately after preparation	a month later	2 months later	6 months later	A year later
Example 1	580g	90	92	88	91	89
Example 2	580g	91	90	89	91	92
Example 3	435g	89	88	90	98	91
Example 4	435g	92	87	90	90	88
Comparative Example 1	300ml	89	90	91	90	87

As is shown above, the water dispersible granule according to the examples effect

on barnyard millets after long-term storage like the products of the comparative examples. Therefore, it has no problem related to long-term storage.

Storage Stability Test

5 To confirm the storage stability of the product according to the examples, time course test was carried out at 15 °C and 50 °C. The result are disclosed in following Table 7

Table 7. Test Result of the Water Dispersible Granule according to the Examples

	Storage Temperat -ure	Net content of paraquat(%)					
		Imme -diately preparat -ion	A week later	4 weeks later	8 weeks later	16 weeks later	32 weeks later
Example 1	15°C	12.8	12.8	12.8	12.8	12.8	12.8
	50°C	12.8	12.8	12.8	12.7	12.7	12.6
Example 2	15°C	12.8	12.8	12.8	12.8	12.8	12.8
	50°C	12.8	12.8	12.8	12.8	12.7	12.7
Example 3	15°C	17.0	17.0	17.0	17.0	17.0	17.0
	50°C	17.0	16.9	16.9	16.9	16.9	16.7
Example 4	15°C	17.0	17.0	17.0	17.0	17.0	17.0
	50°C	17.0	17.0	17.0	16.9	16.8	16.8

10 As is shown above only, less than 2% of Paragat in the water dispersible granule prepared according to the present invention was decomposed even after 32 weeks' storage under the harsh condition of 50 °C. So, the composition is stable after the long-term storage.

As is shown from the above test results, the water dispersible granule according to
15 the present invention shows superior effect on barnyard millets, crab grasses, fleabanes,

mugworts and copperleaves. Further, it has the effect of lowering the regenerating ratio of weeds, such as barnyard millets, crab grasses, fleabanes, mugworts and copperleaves that have high regenerating ratio. Further, it has agrichemical effect stability and storage stability even after long-term storage.

5

Industrial Applicability

The water dispersible granule according to the present invention is prepared by mixing and kneading paraquat, surfactant, breakage promoter and extender, forming
10 granules out of kneaded mixture, and drying the granules.

It can prevent the danger of poisoning caused by contact or ingestion when conventional soluble concentrate or wettable powder is used, and of poisoning due to intake by accident or on purpose.

Further, the water dispersible granule according to the present invention maintains
15 its effect after long-term storage. So, it can remove the weeds on ridgeway or non-farm land effectively. Further, it has fast effect as the soluble concentrate of paraquat, so it can remove the weeds only 3 days after treatment.

Though the present invention was described in detail with specific embodiments, it is obvious that the present invention can be modified and corrected variously within the
20 scope of its technical concept. And it is also obvious that such modification and correction fall within the appended claims.

WHAT IS CLAIMED IS:

1. Water dispersible granule containing paraquat comprising 5-50wt% of Paraquat Dichloride, 5-30wt% of surfactant, 1-20wt% of breakage promoter and the rest of extender, wherein said water dispersible granule is prepared by mixing the above
5 components, kneading mixture together with a small amount of water, forming granules out of kneaded mixture using a granulator or the like and drying the granules.
2. Water dispersible granule according to Claim 1, wherein said surfactant is anionic surfactant and/or nonionic surfactant.
- 10 3. Water dispersible granule according to Claim 1, wherein said breakage promoter is at least one selected from the group consisting of sodium sulfate, sodium nitrate, potassium chloride, ammonium sulfate, urea, polyvinylpyrrolidone and the like.
4. Water dispersible granule according to Claim 1, wherein said extender is at least one selected from the group consisting of diollite, kaolin, clay, white carbon,
15 watersoluble starch, calcium carbonate, bentonite, pyrophyllite, talc and the like.
5. A preparing method of water dispersible granule containing paraquat comprising:
 - a) mixing paraquat dichloride, surfactant, breakage promoter and extender, and kneading mixture together with 1-15wt% of water for the mixture at room temperature for 10min-1hr;
 - 20 b) forming granules out of product of step a) using a granulator; and
 - c) drying product of step b) in a fluidized bed dryer at 70-150°C for 10min-1hr.

INTERNATIONAL SEARCH REPORT

national application No.

PCT/KR00/01051

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 A01N 25/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(7) A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patent and application for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
IPN, NPS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,635,445 A (CFPI) 03 JUNE 1997	1
A	see the whole document	2-5
A	JP 11-199409 A (ISSAN CHEM IND LTD) 27 JULY 1999	1-5
	see the whole document	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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